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A Crystalline Monomeric Allenyl/Propargyl Radical

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Supporting Information Placeholder

ABSTRACT: Reduction of alkynyl iminium salts derived from cyclic (alkyl)(amino)carbenes (CAACs) affords propargyl/allenyl radicals. Depending on the nature of the CAAC and alkyne substituents, these radicals can irreversibly dimerize, exist as monomers in solution but dimerize in the solid state, or can even remain monomeric as solids. The first characterization of an allenyl radical by single crystal X-ray crystallography is reported.

Organic open shell molecules play a fundamental role in several areas of chemistry and biology, but their inherent high reactivity and thermal instability make them challenging targets for isolation.[1] α-Amino radicals have been postulated as key intermediates in various chemical transformations, such as photo-redox catalytic processes.[2,3] Although these radicals benefit from electron delocalization, they are usually not isolable and, even with the help of the capto-dative effect,[4] they still dimerize in the solid state as illustrated by the well-known 2-oxomorpholin-3-yl radical **I** (Figure 1).[5] Recently, our group and others have shown that cyclic (alkyl)(amino)carbene (CAAC)[6,7] scaffolds are excellent for stabilizing a variety of main-group and transition metal paramagnetic species,[8,9] and of particular interest, they allow for the isolation of carboxy radicals **II**.[10] The next question was whether the capto-dative effect was a requirement for the isolation of CAAC-derived carbon-centered radicals. To address this question, we chose allenyl/propargyl radicals, depending on which canonical form is drawn, as targets.[11] The parent compound **III**[12] has been widely studied because its dimerization is believed to be responsible for the formation of benzene in combustion processes.[13] Even more sterically protected propargyl radicals such as **IV** are known to spontaneously give rise to the propargyl/propargyl and propargyl/allenyl dimers **Va** and **Vb**, respectively.[14] However, this class of radicals has been detected by EPR, but only in argon matrices below 100 K.[15] Yet again, even the introduction of an amino group does not allow for the isolation of radicals of type **VI**. Indeed, their EPR spectra could only be recorded by irradiation of the respective propargylic amines and di-butylperoxide in the spectrometer cavity.[16]

Herein we show that providing the right set of substituents, the pyrrolidine scaffold makes allenyl radicals stable at room temperature, and even allow for their isolation in the solid state.

To access the desired allenyl radicals, we chose the reduction method already used for carboxy radicals **II**.[10] The desired alkynyl-iminium precursor **3a** was prepared in two steps (Scheme 1). As recently reported by Turner[17] and our group,[18] CAACs readily activate s*p*-hybridized C-H bonds at room temperature,[19] which allows for the installation of an alkyne fragment. Subsequently, hydride abstraction from **2a** with a stoichiometric amount of DDQ, then followed by treatment with $NOSbF_6$, afforded iminium **3a** in good yield.

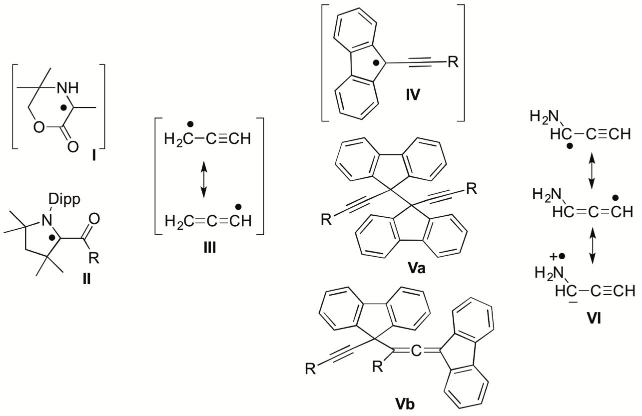
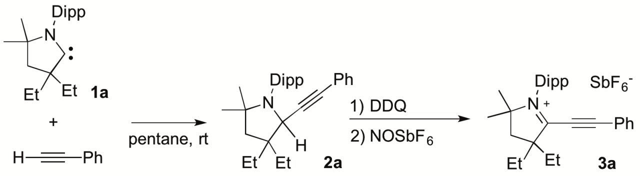


Figure 1. 2-oxomorpholin-3-yl radical **I** which dimerizes in the solid state, CAAC-stabilized carboxy radicals **II**, parent allenyl/propargyl radical **III**, and (amino)allenyl radicals **IV**.



Scheme 1. Synthesis of (alkynyl)iminium salt 3a.

The cyclic voltammogram of **3a** showed a reversible one electron reduction at $E_{1/2}$ = -1.16 V vs. Fc^+/Fc (Figure 2). Upon chemical reduction with one equivalent of cobaltocene, or half an equivalent of tetrakis(dimethylamino)ethylene, a red colored solution, sensitive to air, was obtained. The EPR spectrum confirmed the generation of a paramagnetic species (**4a**) (see SI), which proved to be short-lived at room temperature (Scheme 2). This species dimerizes over a few hours via the allenyl carbon giving **5a**. Note that this allenyl/allenyl dimer is different from the dimerization product of **IV**,[14] due to the protection provided by the CAAC scaffold. Interestingly, radical **4a** can be trapped by a second equivalent of cobaltocene to give **6a**. For both **5a** and **6a**, the structural connectivity could clearly be established by single crystal X-ray diffraction studies (Figure 3).

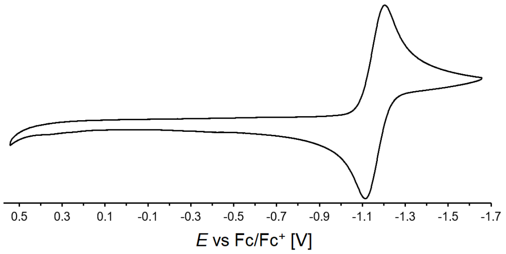
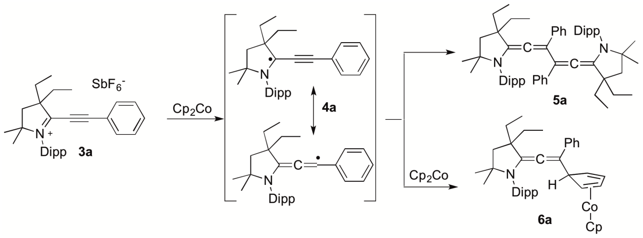


Figure 2. Cyclic voltammogram of (alkynyl)iminium salt **3a**. (nBu_4NPF_6 0.1M in THF, 100 mVs^{-1}, vs. Fc$^+$/Fc).



Scheme 2. Synthesis of short-lived (amino)allenyl radical 4a, its dimer 5a and trapping product 6a.

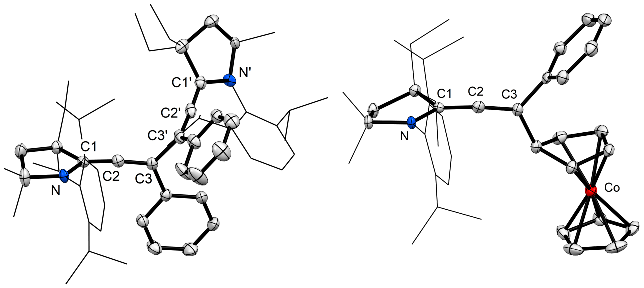


Figure 3. Solid-state structures of dimer **5a** (left) and cobaltocene adduct **6a** (right). Selected bond lengths [Å] and angles [°]: **5a** N-C1 1.412(4); C1-C2 1.311(4); C2-C3 1.319(4); C3-C3' 1.544(4), C1-C2-C3 170.7(3); **6a** N-C1 1.3947(17); C1-C2 1.3194(19); C2-C3 1.3148(19); C1-C2-C3 166.84(14).

In the hope of preventing this dimerization process, we protected the allenyl position using a CAAC precursor that features the bulky menthyl group. Upon reduction of **3b** with cobaltocene, a red solution was obtained which appeared to be EPR active (Figure 4). Simulation[20] [a_N = 4.3 G; a_H = 2.9 G; a_H = 0.5 G; a_H = 2.8 G; a_H = 2.3 G] and DFT calculations of the EPR parameters are in agreement with the desired radical species **4b** (see SI). Note that in addition to the expected hyperfine couplings with N and the *ortho*, *meta* and *para* Hs, there is a coupling with one H atom of the menthyl group; the latter is predicted by DFT. The spin density is delocalized on the nitrogen, the propargyl and the allenyl carbons as well as on the *para* and *ortho* positions of the benzene ring (see SOMO). In contrast to **4a,** radical **4b** is stable in solution for days. However, attempts to obtain single crystals led to the dimeric species **7b**. Because of the steric protection by the menthyl group, the formation of the allenyl-allenyl dimer, analogous to **5a**, does not occur. Instead, the dimerization involves an allenyl carbon of one molecule and the *para*-carbon of the phenyl group of a second molecule, a process reminiscent to the dimerization of Gomberg radical.[21] Dissolving yellow crystals of **7b** in THF gave back a red solution, which gives an EPR signal identical to that observed for **4b**.

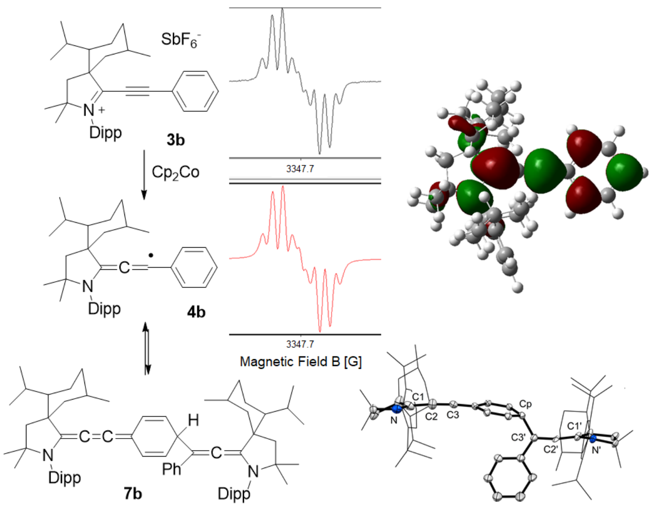
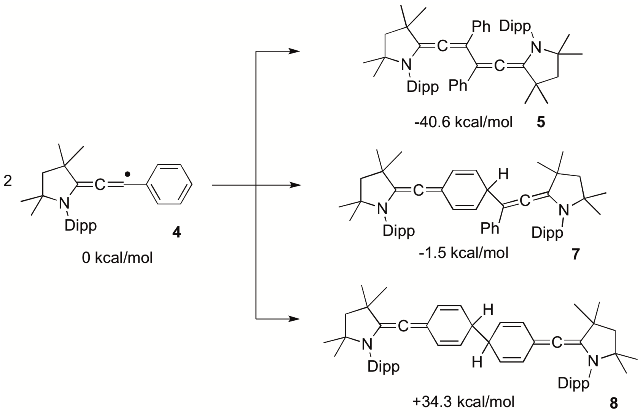


Figure 4. Synthesis of (amino)allenyl radical **4b**, its experimental and simulated EPR spectra, its calculated SOMO, and the solid-state structure of its dimer **7b**.

We investigated the different dimerization pathways by DFT calculations using the model compound **4** (Scheme 3). The allenyl-allenyl dimerization process giving **5** is energetically highly favorable (ΔG = -40.6 kcal/mol). The dimerization that involves the allenyl and the *para*-benzene carbons to afford **7** is almost thermo-neutral as a result of the loss of aromaticity (ΔG = -1.5 kcal/mol). This value readily rationalized the experimentally observed monomer/dimer **4b**/**7b** equilibrium. Note that the *para*-*para* benzene dimerization that leads to **8** is highly unfavorable (+ 34.3 kcal/mol) as two benzene rings are de-aromatized.



Scheme 3. Dimerization pathways for model (amino)allenyl radical 4 with free Gibbs energies calculated at the B3LYP-D3/cc-pVDZ level.

To inhibit the dimerization processes observed with **4b**, we first replaced the phenyl substituent with a *tert*-butyl group. Reduction of the corresponding iminium salt afforded **4c** (Figure 5). This allenyl radical is perfectly stable in solution for days, but all attempts to obtain single crystals suitable for an X-ray diffraction study failed.

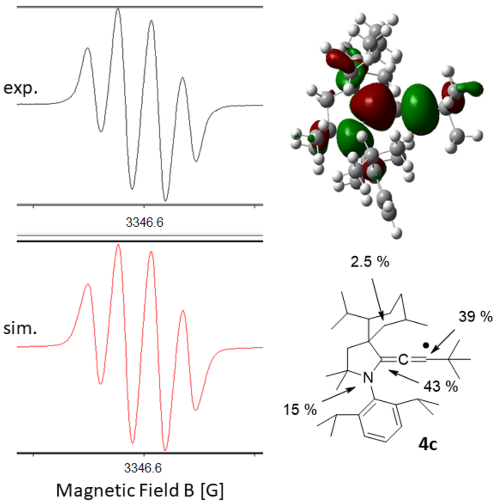


Figure 5. Experimental and simulated EPR spectra (a_N = 4.42 G, a_H = 3.76 G) of **4c**, with the SOMO and Mulliken spin densities calculated at the UB3LYP/def2-TZVP level.

Tert-butyl and menthyl groups are notorious for making crystallization difficult, and thus we moved to a trityl substituent at the alkyne moiety and ethyl groups on the CAAC. To our delight, reduction of the corresponding iminium salt led to radical **4d**, which was fully characterized in solution, but also in the solid state thanks to single crystals obtained from a pentane solution at -40 °C (Figure 6). Not surprisingly, when compared to the iminium precursor **3d**, there is a considerable lengthening of the N-C1 bond distance [**3d**: 1.281(9), **4d**: 1.3850(14) Å]. More interestingly, the C1-C2 [**3d**: 1.430(10), **4d**: 1.3821(17) Å] and C2-C3 [**3d**: 1.178(9), **4d**: 1.2191(17) Å] bond are shorter and longer, respectively. This highlights the importance of the allenyl resonance form, which is confirmed by the calculated SOMO and Mulliken spin densities.

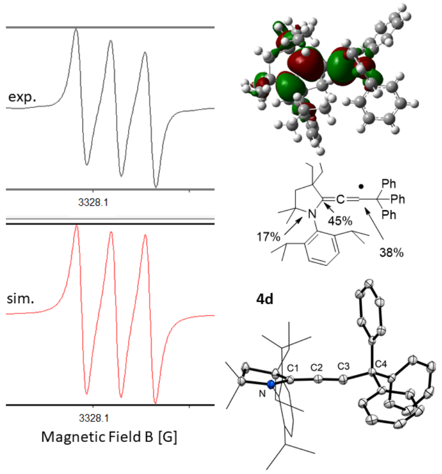


Figure 6. Experimental and simulated EPR spectra (a_N = 4.45 G), SOMO and Mulliken spin densities calculated at the UB3LYP/def2-TZVP level, and solid-state structure of **4d**. Selected bond lengths [Å] and angles [°]: N-C1 1.3850(14); C1-C2 1.3821(17); C2-C3 1.2191(17); C3-C4 1.4847(18), C1-C2-C3 177.7(12); C2-C3-C4 163.37(12).

The isolation of the first CAAC-derived α-amino radicals, not stabilized by capto-dative effects, demonstrates the effectiveness of the pyrrolidine scaffold, bearing bulky substituents, to stabilize paramagnetic species. Importantly, this class of compounds is readily accessible in three-steps from cyclic (alkyl)(amino)carbenes. We are currently using these stable versions of α-aminoalkyl radicals to gain further insight into the mechanism of photoredox catalytic reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/xxx. CCDC 1573244 (**3a**), 1573245 (**4d**), 1573246 (**5a**), 1573247 (**7b**), 1573248 (**3d**), 1573249 (**6a**) contain the crystallographic data.

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Notes

The authors declare no competing financial interests.

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